Hartree-Fock Theory

ISTPC
Summer School
June 19th - July 1st 2022 Aussois

Vincent Robert, vrobert@unistra.fr

UdS - UMR 7177 Laboratoire de Chimie Quantique

Université de Strasbourg

FRC International Center for Frontier Research in Chemistry

Institut de Chimie de Strasbourg UMR 7177

1. N-electron problem
2. Independent electron approximation
   - Non-interacting electrons
   - Orbitals (*AOs* and *MOs*)
   - Electron-electron interactions
   - Self-Consistent Field Method
   - Slater determinant
   - Hartree-Fock equations
   - Roothan equations - atomic basis sets
   - A featuring system : H_2
3. General results : Brillouin, Koopmans' theorems
4. Beyond Hartree Fock : Configuration Interaction
5. Conclusions

N-electron Problem

N electrons $\rightarrow \{i\}$ light particles
M ions $\rightarrow \{A\}$ heavy particles

$$\hat{\mathcal{H}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

$m_i/M_A \approx 1/2000$
frozen ions : Born-Oppenheimer approximation

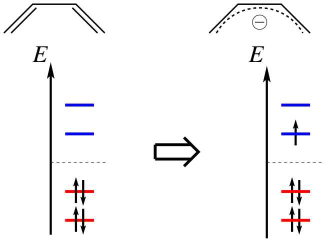
$\frac{1}{r_{ij}} \rightarrow$ NON-INDEPENDENT particles !

APPROXIMATED SOLUTION

Non-interacting electron Case

"$\frac{1}{r_{ij}} = 0$"

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{h}(i) \quad \rightarrow \quad E_0 = \sum_{i=1}^{N} \epsilon_i$$



$$\boxed{E(N+1) = E(N) + \epsilon_{N+1}}$$

convenient and simple, though approximate !

Digression : Hückel Theory

semi empirical method for π-conjugated hydrocarbons

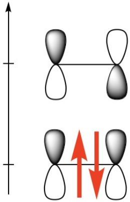
$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{h}(i) \quad \rightarrow \quad \Psi(r_1, r_2, ...r_N) = \prod_{i=1}^{N} \varphi(r_i)$$

$$\begin{aligned} \langle \varphi_i | \hat{h} | \varphi_i \rangle &= \alpha \sim -10eV \quad \leftarrow \quad \textit{Coulomb} \\ \langle \varphi_i | \hat{h} | \varphi_j \rangle &= \beta \ \textit{ or } \ t \sim -1eV \quad \leftarrow \quad \textit{resonance} \\ \langle \varphi_i | \varphi_j \rangle &= \delta_{ij} \end{aligned}$$

example : ethylene, 2AOs $\rightarrow$ 2MOs

$\epsilon_b = \alpha + \beta \qquad \epsilon_a = \alpha - \beta$

$\Delta E = 2|\beta| = h\nu \rightarrow$ parametrization



Digression : Hückel Theory

comments (see Nathalie Guihéry's lecture)

- effective electron-electron repulsion
- qualitative MOs : nodal structure
- energetics : one-electron picture !

BUT

- *transferability* of parameters ?
- steric *hindrance* ?
  $\Delta E(4e) = 2(\alpha + \beta) + 2(\alpha - \beta) - 4\alpha = 0$!

Orbital Approximation

"electrons in boxes"

Atomic Orbitals → *Molecular* Orbitals

ORBITAL : eigenfunction of a *monoelectronic* problem

$$\hat{h}\varphi = \epsilon\varphi \qquad \|\varphi\|^2 = \int \varphi^* \varphi dr = \langle\varphi|\varphi\rangle = 1$$

Linear Combination of Atomic Orbitals (*LCAO*)

$$\psi_{MO} = \sum_{i=1}^{N} c_i \varphi_i$$

example 1 : Hückel for conjugated systems

$\{2p_z\}$ SIMPLE ZETA

example 2 : *extended* Hückel

$\{AO\}_i$ MULTIPLE ZETA

$\varphi_i = a_1 exp\{-\zeta_1 r\} + a_2 exp\{-\zeta_2 r\}$

how do the electrons see each other ?

Electron-Electron Interactions

"$\frac{1}{r_{ij}} \neq 0$"

Hartree's assumptions :

1. instantaneous interaction $\rightarrow$ average interaction
spherical for atoms

2. *self-consistency*

$$\{\varphi_i\} \rightarrow \text{Coulomb} \rightarrow \hat{h}\tilde{\varphi}_i = \epsilon_i \tilde{\varphi}_i \rightarrow \{\tilde{\varphi}_i\}$$

$$\|\tilde{\varphi}_i - \varphi_i\| \rightarrow 0$$

3. Pauli *exclusion* principle
"no two electrons with same spin in the same orbital"

$\rightarrow$ *spherical averaging* of the Coulomb potential

Self-Consistent Field Method

atomic calculations

- the electrons move *independently* one from the other :

$$\Psi(\{r_i\},\{\theta_i\},\{\phi_i\}) = \varphi_1(r_1,\theta_1,\phi_1)\cdots\varphi_N(r_N,\theta_N,\phi_N)$$

$\rightarrow$ Hartree product

- let us write as for the hydrogen atom :

$$\varphi(r,\theta,\phi) \;=\; \frac{P(r)}{r} Y_l^m(\theta,\phi)$$

$Y_l^m(\theta,\phi)$: spherical harmonics (*e.g.* $Y_0^0(\theta,\phi)\hat{=}1s$)

$$\hat{\mathcal{H}} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{j>i}\frac{1}{r_{ij}} = \sum_i f_i + \sum_{j>i} g_{ij}$$

- electrostatic part $\sum_{j>i} g_{ij}$:

$$\int \varphi_i^*(r_1)\varphi_j^*(r_2)\frac{1}{r_{12}}\varphi_i(r_1)\varphi_j(r_2)\mathbf{dr}_1\mathbf{dr}_2 = (ii,jj)$$

: *Coulomb integral*

Spherical Averaging : Hartree's equations

$$\boxed{\delta\langle\psi|\hat{\mathcal{H}}|\psi\rangle_{av} = 0}$$

- averaging the charge distribution around r_1 :

$$\delta Q(r_1) = P_j^2(r_1)dr_1$$

- energy at r_2 : $\frac{\delta Q(r_2)}{r_1}$ if $r_1 > r_2$ and $\frac{\delta Q(r_2)}{r_2}$ if $r_1 < r_2$

$$Y_0(r_1, j) = \frac{1}{r_1}\left\{\int_0^{r_1}\delta Q(r_2)dr_2 + \int_{r_1}^{\infty}\delta Q(r_2)\frac{r_1}{r_2}dr_2\right\}$$

- *spherically averaged* ith and jth charge distributions :

$$F_0(i,j) = \int_0^{\infty}\delta Q(r_1)Y_0(r_1,j)dr_1 = \int_0^{\infty}\int_0^{\infty}\delta Q(r_1)\frac{1}{r_{max}}\delta Q(r_2)$$

$$\boxed{\left\{-\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} - \frac{Z^*}{r}\right\}P_i(r) = \epsilon_i P_i(r)}$$

$$Z^* = Z - \sum_{j\neq i} Y_0(r_i, j)$$: *screening* effect

Antisymmetry of the Wave Function

2-electron system

- experimental facts : $1s2s \rightarrow$ *antisymmetric* ^1S
  and *symmetric* ^3S

- triplet/singlet spin parts : symmetric/antisymmetric
  $M_S = 0$ component : $\alpha(1)\beta(2) \pm \alpha(2)\beta(1)$

  triplet : ↑ ↓ + ↓ ↑

Slater determinant

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) \end{vmatrix} \quad \text{with} \quad \boxed{x_i = (r_i, \omega_i)}$$

Note : $\varphi_{i,j}$ = *spin-orbitals*

- antisymmetry : $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$

- Pauli's principle verified : $\Psi(x, x) = 0$ (identical lines !)

Properties-Generalization

$\varphi(x_i) = \varphi(r_i)\alpha(\omega_i)$ or $\varphi(r_i)\beta(\omega_i)$

- Space parts of the wave-functions :

$|S=1, M_S=0\rangle = \varphi_i(r_1)\varphi_j(r_2) - \varphi_i(r_2)\varphi_j(r_1)$

$|S=0, M_S=0\rangle = \varphi_i(r_1)\varphi_j(r_2) + \varphi_i(r_2)\varphi_j(r_1)$

$r_1 \neq r_2$ in the triplet

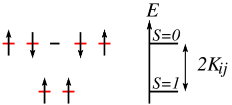
- Coulomb interactions larger in $S=0$ than in $S=1$

- Analytically, $E_0 - E_1 = 2K_{ij}$

with $K_{ij} = \int \varphi_i^*(r_1)\varphi_j^*(r_2)\frac{1}{r_{12}}\varphi_i(r_2)\varphi_j(r_1)\mathbf{dr}_1\mathbf{dr}_2$

$= \langle ij|1/r|ji\rangle = (ij, ji)$: *exchange integral*

$\rightarrow$ Hund's rule : S_{max} is favored



Generalization : Slater determinant

Starting from 2-electron functions :

$$\Psi_1(x_1, x_2) = \varphi_i(x_1)\varphi_j(x_2) \quad \Psi_2(x_1, x_2) = \varphi_j(x_1)\varphi_i(x_2)$$

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) \end{vmatrix}$$: Slater determinant

More generally :

$$\Psi(\{x_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) & \cdots & \varphi_k(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) & \cdots & \varphi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \varphi_i(x_N) & \varphi_j(x_N) & \cdots & \varphi_k(x_N) \end{vmatrix}$$

notation : $\Psi = |\varphi_i \varphi_j \cdots \varphi_k|$

$\{\varphi_j\}$ = *orthonormal* molecular spin-orbital basis set

Hartree-Fock Equations

$$E[\{\varphi_a\}] = \langle\psi|\hat{\mathcal{H}}|\psi\rangle \text{ and } \langle\psi|\psi\rangle = 1$$

(i) single Slater determinant : $\Psi = |\varphi_1\varphi_2\cdots\varphi_a\varphi_b\cdots\varphi_N|$

(ii) $\delta E = 0$ under the constraints $\langle\varphi_a|\varphi_b\rangle = \delta_{ab}$

$$\mathcal{L}[\{\varphi_a\}] = E[\{\varphi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N}\epsilon_{ba}(\langle\varphi_a|\varphi_b\rangle - \delta_{ab})$$

$$\Longrightarrow \boxed{\hat{\mathcal{F}}(1)\varphi_i(1) = \epsilon_i\varphi_i(1)}$$

: Hartree-Fock equations ($\sim$ 1930)

$\hat{\mathcal{F}}$ = Fock operator $\rightarrow$ *monoelectronic*

$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_{a,\text{occupied}} \hat{J}_a(1) - \hat{K}_a(1)$$

$$\hat{J}_a(1) = \int dx_2\varphi_a^*(2)r_{12}^{-1}\varphi_a(2)$$

$$\hat{K}_a(1)\varphi_i(1) = \left[\int dx_2\varphi_a^*(2)r_{12}^{-1}\varphi_i(2)\right]\varphi_a(1)$$

$\hat{J}_a$ = Coulomb, LOCAL $\quad$ $\hat{K}_a$ = exchange, NON-LOCAL

Coulomb, Exchange Operators, Hartree-Fock Potential

Coulomb $\hat{J}_b$

$$\langle a|\hat{J}_b|a\rangle = \int dx_1 dx_2 \varphi_a^*(1)\varphi_b^*(2) r_{12}^{-1}\varphi_b(2)\varphi_a(1) = (aa,bb) = J_{ab}$$

exchange $\hat{K}_b$

$$\langle a|\hat{K}_b|a\rangle = \int dx_1 dx_2 \varphi_a^*(1)\varphi_b^*(2) r_{12}^{-1}\varphi_a(2)\varphi_b(1) = (ab,ba) = K_{ab}$$

$\langle\alpha|\beta\rangle = 0 \Rightarrow K_{ab} = 0$ for electrons of opposite spins

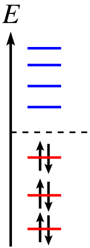
HF potential $\hat{v}_{HF} = \sum_{occ} \hat{J}_b - \hat{K}_b$

$$\langle a|\hat{v}_{HF}|a\rangle = \sum_{b,occ} (aa,bb) - (ab,ba)$$

$\rightarrow \alpha$ and β electrons are not *correlated*

Properties-Resolution

- α and β electrons form two discernable sets ($\hat{K}$ operator $\rightarrow$ spin *polarization*)



- closed-shell systems : *Restricted Hartree-Fock*

$$\hat{\mathcal{F}}(1) = \hat{h}(1) + \sum_{\textbf{MOs}}^{N/2} 2\hat{J}_a(1) - \hat{K}_a(1)$$

- $\langle a|\hat{J}_a|a\rangle = \langle a|\hat{K}_a|a\rangle$
cancellation in $\hat{v}_{HF}$: no *self-interaction*

- $\hat{\mathcal{F}} = f\left(\{\varphi_a, occ\}\right) \Rightarrow$ *iterative* resolution until *self-consistency* : $\langle i|\hat{\mathcal{F}}|j\rangle = \delta_{ij}\epsilon_i$

- along the HF procedure $\frac{1}{r_{12}} \rightarrow \hat{v}_{HF}$: *mean field*

Roothaan Equations

introduction of a basis LCAO

$$\varphi_i = \sum_{\mu=1}^{M} c_{\mu i} \chi_\mu \quad M \sim 1000$$

two $M \times M$ matrices must be introduced :

$$S_{\mu\nu} = \int dr_1 \chi^*_\mu(1) \chi_\nu(1) \;\; : \text{metric}$$

$$F_{\mu\nu} = \int dr_1 \chi^*_\mu(1) \mathcal{F}(1) \chi_\nu(1) \;\; : \text{Fock matrix}$$

$$\sum_\mu F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu} c_{\nu i}$$

$$\boxed{FC = SC\epsilon} \quad : \text{Roothaan equations}$$

Roothaan Equations in Practice

non-orthogonal atomic orbitals

- Slater type (*atomic-like*)
  example : double dzéta, DZ

$$\varphi_i(r) = a_1 exp\{-\zeta_1 r\} + a_2 exp\{-\zeta_2 r\}$$

- Gaussian type and contractions
  - minimal basis sets Slater $\leftarrow$ linear combination of Gaussians

$$\varphi_i(r) = \sum_i c_i exp\{-\alpha_i r^2\}$$

  - *contraction* : some of the coefficents are frozen
    example : 6-31G
    6 for the core
    $3 + 1$ for the valence $\rightarrow$ *split valence*

Unrestricted Hartree-Fock

different α and β spatial forms

$$\hat{\mathcal{F}}_\alpha(1) = \hat{h}(1) + \sum_{\mathbf{N}_\alpha} \left[\hat{J}_{a,\alpha}(1) - \hat{K}_{a,\alpha}(1)\right] + \sum_{\mathbf{N}_\beta} \hat{J}_{a,\beta}(1)$$

$J_{ij}^{\sigma\sigma}, K_{ij}^{\sigma\sigma}$ and $J_{ij}^{\alpha\beta}$: coupling between $\hat{\mathcal{F}}_\alpha$ and $\hat{\mathcal{F}}_\beta$!

How to practically solve $FC = SC\epsilon$?
Find X such as $X^\dagger SX$ diagonal $\rightarrow X = S^{-\frac{1}{2}}$

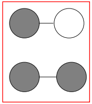
$$\boxed{F'C' = C'\epsilon} \text{ with } F' = X^\dagger FX$$

$\rightarrow$ "standard" *eigen-value problem*

Main drawback of UHF method : $\langle \hat{\mathcal{S}}^2 \rangle \neq S\,(S+1)$
$\rightarrow$ *spin contamination* issue

H_2 as an example

- *minimal* basis set : $\{1s_a, 1s_b\} = \{a, b\}$



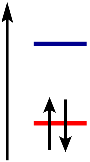
$$\varphi_1 = \xi_1 a + \xi_2 b$$
$$\varphi_2 = \xi_2 a - \xi_1 b$$

from *group theory*, $|\xi_1| = |\xi_2| = \frac{1}{\sqrt{2}}$

$$\varphi_1 = g \text{ and } \varphi_2 = u$$

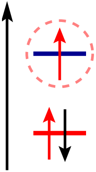
- *self-consistency* is automatically achieved

$$F_{gu} = \langle u|\hat{\mathcal{F}}|g\rangle = 0 \quad F_{gg} = \langle g|\hat{\mathcal{F}}|g\rangle = \epsilon_g \quad F_{uu} = \langle u|\hat{\mathcal{F}}|u\rangle = \epsilon_u$$



$\epsilon_u = \,?$ $\quad E_{HF} = f\,(\epsilon_g, \epsilon_u)\,?$

$$\boxed{\epsilon_g = h_{gg} + J_{gg}}$$



$$\boxed{\epsilon_u = h_{uu} + 2J_{gu} - K_{gu}}$$

Hartree-Fock Energy

$$\boxed{E_{HF} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle} \quad \text{with } \Psi = |a\bar{a}\cdots|$$

from a "natural" inspection : $E_{H_2} = 2h_{gg} + J_{gg}$

How does this compare to $2\epsilon_g$?

$$E_{H_2} = 2\epsilon_g - J_{gg} \Rightarrow \qquad E_{HF} \neq \sum_{a,occ} \epsilon_a \ !$$

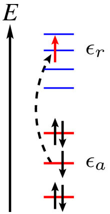
$$E_{HF} = \sum_{a,occ} h_{aa} + \frac{1}{2} \sum_{a,b} \Big[(aa,bb) - (ab,ba) \Big] \quad \leftarrow \text{ Slater's rules}$$

$$= \sum_{a,occ} \epsilon_a - \frac{1}{2} \sum_{a,b} \Big[(aa,bb) - (ab,ba) \Big]$$

$$-\frac{1}{2} \sum_{a,b} \Big[(aa,bb) - (ab,ba) \Big]$$

avoids *double counting* of *e*-*e* interactions

Brillouin and Koopmans' Theorems

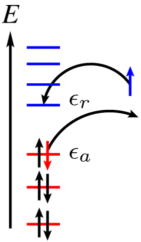


Single Excited Determinants

$$|\Psi_a^r\rangle = a_r^\dagger a_a |\Psi_{HF}\rangle$$

$$\langle\Psi_{HF}|\hat{\mathcal{H}}|\Psi_a^r\rangle = 0$$

What do we learn from the ϵ_i ?

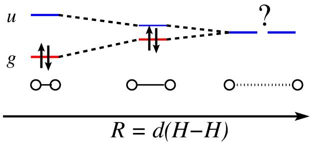


$$eA = -\epsilon_r \qquad eA = {}^{N}E_{HF} - {}^{N+1}E_r$$

$$IP = -\epsilon_a \qquad IP = {}^{N-1}E_a - {}^{N}E_{HF}$$

ϵ_i calculated for the *N-electron* system !

Pathology of the Hartree-Fock Solution



H_2 DISSOCIATION

Does $\Psi_{HF} = |g\bar{g}|$ survive as $R \to \infty$?

Since $g = \frac{1}{\sqrt{2}}(a+b)$, $\Psi_{HF} = \frac{1}{2}\left[\left(|a\bar{a}| + |b\bar{b}|\right) + \left(|a\bar{b}| + |b\bar{a}|\right)\right]$

$$\boxed{\Psi_{HF} = \frac{1}{\sqrt{2}}\left[\Psi_{ionic} + \Psi_{neutral}\right]}$$

incompatible with $\Psi \approx \Psi_{neutral}$ as $R \to \infty$!

$\Rightarrow$ "suppress" the *ionic contributions* : $\boxed{\Psi = \lambda|g\bar{g}| - \mu|u\bar{u}|}$

Hartree-Fock invalidated : *beyond mean field* is necessary...

Configuration Interaction

Let us analyze $\Psi = \lambda|g\bar{g}| - \mu|u\bar{u}|$
λ and μ are determined variationally

$g = \frac{1}{\sqrt{2}}(a+b)$ and $u = \frac{1}{\sqrt{2}}(a-b)$

$\Psi = \frac{\lambda-\mu}{2}\left(|a\bar{a}| + |b\bar{b}|\right) + \frac{\lambda+\mu}{2}\left(|a\bar{b}| - |\bar{a}b|\right)$
asymptotically, $\lambda - \mu \to 0$ as $R \to \infty$

$\{|g\bar{g}|, |u\bar{u}|\}$ define the basis set :

$\boxed{\langle g\bar{g}|\hat{\mathcal{H}}|u\bar{u}\rangle = (gu, ug) = K_{gu}}$ and $\boxed{E_{u\bar{u}} - E_{g\bar{g}} = 2\Delta}$

configuration interaction matrix :

$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{HF} + 2\Delta \end{pmatrix}$$

Correlation Energy and Wavefunction Expansion

definition : $E_{corr} = E - E_{HF}$

E_{corr} from the diagonalization of :

$$\begin{pmatrix} E_{HF} & K_{gu} \\ K_{gu} & E_{HF} + 2\Delta \end{pmatrix}$$

The expansion of the lowest root leads to :

$$E_{corr} = -\frac{K_{gu}^2}{2\Delta} + O\left(\frac{K_{gu}^3}{\Delta^2}\right)$$

and

$$\Psi = |g\bar{g}| - \frac{K_{gu}}{2\Delta}|u\bar{u}| = \Psi_{HF} + c^{(1)}|u\bar{u}|$$

$\boxed{c^{(1)} = -\frac{K_{gu}}{2\Delta}}$ first order in *perturbation theory*

Generalization of CI Expansion

From $\quad \Psi = c_0\Psi_0 + \sum_{ar} c_{ar}\Psi_a^r + \sum_{a<b,r<s} c_{ab}^{rs}\Psi_{ab}^{rs} + \ldots$

projection of Schrödinger equation onto $|\Psi_0\rangle$ leads to :

$$E = E_0 + \sum_{a<b,r<s} c_{ab}^{rs}\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle$$

$$\begin{pmatrix}
\Psi_0 & \Psi_a^r & \Psi_{ab}^{rs} & \Psi_{abc}^{rst} & \cdots \\
\langle\Psi_0|\hat{\mathcal{H}}|\Psi_0\rangle & & & & \\
0 & \langle\Psi_a^r|\mathcal{H}|\Psi_a^r\rangle & & & \\
\langle\Psi_0|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle & \langle\Psi_a^r|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle & \langle\Psi_{ab}^{rs}|\hat{\mathcal{H}}|\Psi_{ab}^{rs}\rangle & & \\
0 & 0 & \langle\Psi_{ab}^{rs}|\hat{\mathcal{H}}|\Psi_{abc}^{rst}\rangle & \langle\Psi_{abc}^{rst}|\mathcal{H}|\Psi_{abc}^{rst}\rangle & \\
\vdots & \vdots & \vdots & \vdots & \vdots
\end{pmatrix}$$

- several millions of configurations !
- exponential growth
  → *truncation* : CI Singles Ψ_a^r and Doubles Ψ_{ab}^{rs}
- alternative methods : localization, entanglement

Conclusion and References

- Hartree-Fock as a starting point
- mean-field approximation : orbitals rotation
  orthogonal MOs, Brillouin
- further expansion is necessary
  $\rightarrow$ CASSCF, MCSCF, CISD (Emmanuel Fromager)
- perturbation theory as an alternative
  $\rightarrow$ MP2, MRPT (Pierre François Loos, Celestino Angeli)

References :

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*
J. C. Slater, *Quantum Theory*